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13. ABSTRACT *(Maximum 200 words)*

The primary goal of this study was to determine whether phosphate limitation of phytoplankton occurs in the coastal ocean. Three cruises on the Eel River Shelf, northern California were completed in spring, summer 1996 and winter 1997 from which hydrographic and nutrient inventory data from 3 to 5 shore-perpendicular transects were collected. These geochemical data were coupled with enzymatic assay data for Alkaline Phosphatase (APase), an inducible enzyme indicative of phosphate limitation, to evaluate the importance and spatial distribution of phosphate limitation. Nutrient-nutrient plots (e.g. DIN versus DIP) indicate a shift from N-limitation in spring to P-limitation in summer. Those stations which exhibit lowest DIP in summer also have high APase activities, suggesting that the algal populations at these sites were phosphate limited. These findings indicate that the prevailing dogma of ubiquitous nitrogen (N) limitation of biological productivity in the coastal ocean is overly simplistic. A high degree of spatial variability in surface-water chl-a, dissolved nutrient concentrations, and APase was observed in spring and summer, illustrating the patchy nature of coastal phytoplankton blooms and the importance of high-density sampling grids to effectively characterize the overall biomass and nutrient limitation conditions of such system

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FINAL REPORT

Controls on Bioavailability of Phosphorus in the Coastal Ocean: A Coupled Geochemical and Enzymatic Approach

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LONG-TERM GOAL

My long-term goals are to assess controls on nutrient limitation of biological productivity in the coastal ocean, to identify those processes which control supply of bioavailable nutrients to the coastal ocean, and to critically examine which nutrient(s) limit biological productivity in the coastal ocean. I am particularly interested in assessing the role of phosphorus (P) as a limiting nutrient in the coastal ocean.

OBJECTIVES

Specific objectives were to (1) complete a series of cruises to the Eel River Shelf (spring, summer, winter) plus the coupled river sampling field work, (2) process water column samples taken during these field efforts and during the helicopter rapid-response sampling immediately after the December 1996 Eel River flood, (3) finalize work on method development for Dissolved Organic Phosphorus (DOP) and Alkaline Phosphatase (APase) assays, and (4) combine the geochemical and biological assay data to evaluate the nutrient limitation status of the study area.

APPROACH

I employ geochemical methods to separately quantify dissolved and particulate nutrient pools in river-dominated coastal field areas. The methods employed permit assessment of the size of bioavailable nutrient pools. Changes in the geochemical nature of distinct phosphorus pools along the salinity gradient in the river-dominated coastal zone provide a means for identifying processes which control or otherwise impact the supply of bioavailable nutrients to the coastal ocean. In addition to detailed assessment of phosphorus geochemistry, extensive geochemical characterization of dissolved and particulate matter has further constrained processes affecting supply of phosphorus and other nutrients (nitrogen, silicon, carbon) to this coastal system.

The *in situ* nutrient demand of the phytoplankton community is assessed by determining activity of alkaline phosphatase (APase) in geochemically characterized samples, as described above. The presence of APase activity is a definitive indicator of phosphorus limitation. Biomass is determined by chlorophyll-a analyses. A number of parameters are used in addition to APase activity to assess the limiting nutrient status of the study system (C:N:P ratios, ratios of C, N, and P to Chl-a). These

limiting nutrient indicators are coupled to results of the geochemical analyses described above to identify reservoirs which are actively supplying bioavailable nutrients.

WORK COMPLETED

All field work and analysis of filtered water samples have been completed. Analysis on particulates and bottom sediments has been nearly completed. Analytical work on development and verification of methods for quantifying Dissolved Organic Phosphorus (DOP) is complete and will appear in the Nov. 1999 issue of Limnol. Oceanogr. Optimization of a fluorescence plate reader (a Cytofluor 4000) for analysis of Alkaline Phosphatase (APase) is nearly complete.

RESULTS

Seasonal variability in the nutrient inventories and profile shapes are evident in results from the three STRATAFORM cruises. Dissolved Organic Phosphorus (DOP) constitutes an important fraction of the total dissolved phosphorus inventory in both spring and summer. However, there are important seasonal differences. In the spring, Dissolved Inorganic Phosphorus (DIP) concentrations typically exceed DOP concentrations throughout the water column. Summer profiles, in contrast, show surface water DOP concentrations as much as six times higher than DIP concentrations. These DOP concentration maxima typically coincide with a maximum in chl-a, DIP concentrations near detection limits, and the presence of alkaline phosphatase (APase) activity. The presence of APase activity, an inducible enzyme in algae and bacteria whose presence indicates phosphate limitation, suggests that algae are hydrolyzing DOP to form DIP in order to satisfy their nutritional phosphate demand. The same stations which in summer display higher DOP than DIP and high chl-a often show high surface water ammonia concentrations, as well, resulting in ratios of Dissolved Inorganic Nitrogen (DIN) to DIP which exceed the Redfield Ratio, also consistent with a seasonally phosphate-limited system.

Plots of water column DIN versus DIP indicate a shift from N-limitation in spring to P-limitation in summer, or possibly co-limitation. This trend is not evident if nitrate only is plotted against DIP, demonstrating the importance of including all inorganic nitrogen species in the assessment of nutrient limitation. Ammonia concentrations, in particular, are very high in the summer and drive the system toward phosphate limitation. The relationship between DIN and DIP in these nutrient/nutrient plots is tighter (higher R^2) in spring than in summer. Data from our benthic flux cores indicates that this may be due to the presence of a significant benthic phosphate flux out of sediments in summer.

Results from the January cruise show considerably lower chl-a and higher and more invariant oxygen concentrations, consistent with a lower productivity regime. The water was considerably more turbid than in spring and summer due to the recent flooding of adjacent rivers. Water column DIP from these winter-time samples are remarkably invariant, which may result from the 'phosphate buffering' effect, that is, the sorptive interaction of phosphate with terrigenous particulate matter in the water column.

IMPACT/APPLICATION

Results from the work completed to date suggest that nutrient limitation shifted from Nitrogen (N)-limited in spring to Phosphate (P)-limited in summer on the Eel River Shelf. If this kind of shift is a regular phenomenon in this coastal system, it indicates that current models of nutrient forcing on biological productivity in the coastal ocean may require radical revision. Current models assume ubiquitous N-limitation, and often focus exclusively on nitrate, only one of the possible dissolved and

bioavailable species of N. This work demonstrates the necessity of including all forms of bioavailable nutrients when making an assessment of nutrient limitation of biological productivity.

TRANSITIONS

The uncertainty which exists about which nutrient is 'the' limiting nutrient precludes construction of realistic descriptive or predictive models of coastal ocean biomass dynamics. This has important implications for academic and Naval objectives centered around prediction of biogenic particle production in the coastal ocean. A major objective of this research is to provide evidence of the importance of including 'non-traditional' nutrient pools into productivity-prediction models, and to underline the importance of explicitly documenting the identity of limiting nutrients in a given ecosystem in order to avoid assumptions which may prove unrealistic.

RELATED PROJECTS

This project has benefitted greatly from the opportunity to collaborate with scientists in the ONR-funded STRATAFORM project. In particular, Chuck Nittrouer has been exceedingly helpful in accommodating ship-time needs for carrying out the work described in this report. Nittrouer and other STRATAFORM scientists have expressed interest in the water column data which I am generating as part of this project, as it will help them to constrain the sediment delivery term for strata formation on the Eel River Shelf. In addition, I have been looking at the geochemistry of surface sediments, in particular at components derived from water column productivity, to link surface sediment parameters which provide an indication of organic matter source and reactivity (chl-a, organic C:N:P ratios) to water column profiles of these same parameters. This will provide insight into the seasonal delivery of metabolizable organic matter to the sea bed on the Eel River Shelf. The delivery of water column biogenic particulate matter (e.g. productivity) to the sea bed has a direct effect on strata preservation, through direct sedimentation, and by increasing the supply of reactive organic matter which fuels benthic bioturbating organisms, and promotes sediment reworking and destruction of strata-boundaries.

This project has been succeeded by a subsequent project (Award #: N0-0014-98-1-0169) in which two additional cruises to the Eel River Shelf were completed in an effort to replicate the findings of the initial study. Analysis of these data are underway. A second component to the subsequent study is the examination of existing coastal ocean nutrient data sets for evidence of P-limitation.

PUBLICATIONS

In Press:

Monaghan, E.J. and Ruttenberg, K.C. (1999). Measurement of total dissolved phosphorus in the coastal ocean: A reassessment of available methods and an examination of seasonal water column phosphorus profiles from the Eel River Shelf. Limnol. Oceanogr. (in press for Nov. '99 issue).

In Prep:

Ruttenberg, K.C. (1999). Evidence for a seasonal shift in limiting nutrient status in the coastal ocean.

Ruttenberg, K.C., Haupert, C.L. and Keon, N.E. (1999). Development of a high through-put method for determination of Alkaline Phosphatase in Natural Waters.